

Handwritten: The Chemistry of Germanium

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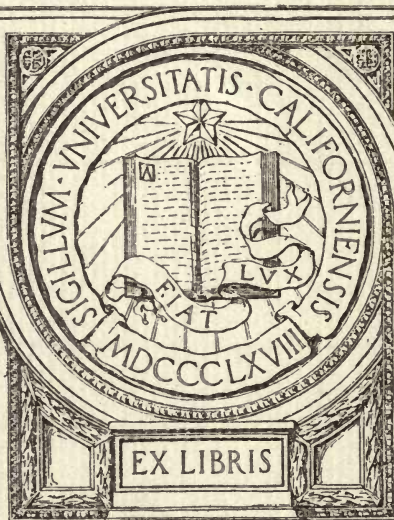


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THE CHEMISTRY OF GERMANIUM



A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL  
OF CORNELL UNIVERSITY FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

FRANK WILLIAM DOUGLAS

September, 1919

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## ACKNOWLEDGEMENT

These investigations were undertaken at the suggestion and under the direction of Professor L. M. Dennis. The author wishes to express his gratitude for the invaluable aid received. He wishes also to acknowledge his indebtedness to Mr. A. W. Bull who assisted in getting the work started; to Mr. R. W. G. Wyckoff for help in making the spectrum analyses and in reading the spectrographs; and, to the New Jersey Zinc Company for the supply of "germanium concentrates" which made the investigations possible.

NOTE: Much of the experimental work, which led to negative results or which the author regards as inconclusive, has been omitted. However the conclusions have, for the most part, been retained. The original thesis is deposited in the library of Cornell University.



# THE HISTORY OF THE UNITED STATES

The history of the United States is a story of the growth of a great nation from a small colony of English settlers. The first settlers came to the New World in search of a better life, and they found it. They built a new society, one of freedom and opportunity, and they made it a reality. The story of the United States is a story of the triumph of the human spirit over adversity, and it is a story that inspires us to this day.

## THE HISTORY AND SOURCES

In 1872 Mendeleef<sup>1</sup> from a vacancy in the carbon group of his periodic table predicted the existence of a new element which he called ekasilicon. Its position in the table lay between silicon and tin. From the properties of elements of the same series, and of the same group, in the periodic table Mendeleeff predicted many of the physical and chemical properties of the element and its principal compounds. These predictions were strikingly verified and the remarkable utility of the periodic table was firmly established by the discovery in 1886<sup>2</sup> of a new element, named by its discoverer Germanium, and a little later recognized by him to be Mendeleeff's ekasilicon.

The element was discovered in a new silver mineral, argyrodite, a silver thio germanate ( $\text{Ag}_4\text{GeS}_4 \cdot 2\text{Ag}_2\text{S}$ ), first found as an incrustation on other silver ores at Freiberg, Germany<sup>3</sup>, and later found in Bolivia<sup>4</sup>. When pure it contained 6.67% of germanium but as it occurred as an incrustation, the germanium content of the Freiberg ore was not greater than 0.36%. This supply is now practically exhausted.

Germanium has also been reported in euxenite<sup>5</sup>, smarskite, tantalite, fergusonite, niobite, gadolinite<sup>6</sup>, canfieldite<sup>7</sup>, frankeite<sup>8</sup>, and in certain zinc blendes<sup>9, 10, 11</sup>.

A recently discovered source of Germanium<sup>12</sup> which appears to be the richest one now available, is a zinc oxide residue, obtained as a by-product in the purification of zinc from certain American ores.

The material used as a source of germanium in the work to be described, was of this character. It was presented to this laboratory by the New Jersey Zinc Company.

<sup>1</sup>Ann., Supp. Bd. 8, (1872), 200.

<sup>2</sup>Clemens Winkler, Ber., 19, (1886), 210.

<sup>3</sup>Jahrb. Miner., (1886) II, 67.

<sup>4</sup>Penfield, Am. J. of Sci., (3) 46, (1893) 107.

<sup>5</sup>Krüss, Ber., 21 (1888) 181.

<sup>6</sup>K. v. Chrustschoff, Z. Krystall., 24, (1895) 516.

<sup>7</sup>Penfield, Am. J. of Sci., (3) 47, (1894) 451.

<sup>8</sup>Stelzner, Jahrb. Miner., (1893) II, 119.

<sup>9</sup>Urbain, Compt. rend., 149, (1909) 602.

<sup>10</sup>Hillebrand and Scherrer, J. Ind. Eng. Chem., 8, (1916) 225.

<sup>11</sup>Buchanan, J. Ind. Eng. Chem., 8, (1916) 585.

<sup>12</sup>Buchanan, J. Ind. Eng. Chem., 9, (1917) 661.

## EXTRACTION OF GERMANIUM

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Winkler<sup>1</sup> fused the finely pulverized argyrodite ore in a Hessian crucible with a mixture of soda and sulphur. The powdered melt was extracted with boiling water. The insoluble residue was repeatedly subjected to the same treatment until free from germanium.

Krüss<sup>2</sup> decomposed euxenite with potassium bisulphate and after extracting the mass with hydrochloric acid, dissolved the germanium with ammonium sulphide.

Urbain<sup>3</sup> Blondel and Obiedoff decomposed zinc blendes by heating with concentrated sulphuric acid, and then extracted the mass with water. The insoluble residue was repeatedly treated by this method until all the germanium was removed.

Buchanan<sup>4</sup> dissolved the zinc oxide in concentrated hydrochloric acid and removed the germanium by distillation in a current of chlorine gas.

Winkler<sup>5</sup> describes a method of fusing the material with potassium carbonate and potassium nitrate, dissolving the mass in water, and after expelling the nitric acid by evaporation with sulphuric acid, diluting and allowing the germanium dioxide to settle out.

Gilchrist, working in this laboratory on the material above described, treated the concentrate, in 15 pound lots, with dilute sulphuric acid (6 N) and enough nitric acid to assure complete oxidation of the germanium. The mass was evaporated to sulphur trioxide fumes in a porcelain lined iron pan. Commercial sulphuric acid was added from time to time until the mass was no longer lumpy. Water was added; the mixture was boiled and allowed to stand until the precipitate settled. The clear liquid was decanted off. The precipitate was extracted by boiling with ammonium sulphate (commercial sulphuric acid and ammonium hydroxide) to dissolve out remaining germanium. The solution was brought to an acidity of six normal, cooled, and saturated with hydrogen sulphide. The precipitate was filtered and converted to oxides by means of concentrated nitric acid and ignition.

<sup>1</sup>J. Prakt. Chem., **34**, (1886) 192.

<sup>2</sup>Ber., **21**, (1888) 131.

<sup>3</sup>Compt. rend., **149**, (1909) 602.

<sup>4</sup>J. Ind. Eng. Chem., **8**, (1916) 585.

<sup>5</sup>J. Prakt. Chem., **36**, (1887) 185.

## Extraction with Dilute Sulphuric Acid and Precipitation with Hydrogen Sulphide.

**Solution of the Concentrates.**—About 42 Kg. of the concentrates was treated in the following manner: approximately six normal sulphuric acid was prepared by mixing in a No. 12 evaporating dish 1 l. of commercial sulphuric acid with 5 l. of water. While the solution was still hot, the concentrates were added, in small portions, with constant stirring. After a few such additions, the temperature rose nearly to the boiling point and effervescence was violent. Addition of concentrates was continued until further additions caused no effervescence. This required about 1.5 Kg.

The precipitate was allowed to settle, and as soon as the dish was cool enough to handle, the solution was filtered using a large Buchner funnel. The rapidity of the extraction depended greatly on the character of these sulphate precipitates. Some were granular, settling rapidly, and filtration was finished in a few minutes. Others were more flocculent and required several hours to complete the filtration. The addition of a little water immediately after the concentrates were dissolved aided in giving a rapid filtration<sup>1</sup>. A spectroscopic test of the precipitate showed zinc, lead, cadmium, and traces of gallium and germanium.

**The Sulphate Precipitates.**—These precipitates, consisting mainly of lead sulphate, were collected and heated in a No. 12 evaporating dish with normal sulphuric acid. The solution was decanted, and the residue was treated with six normal sulphuric acid. The treatment was repeated using N/10 sulphuric acid. The mixture was continuously agitated by means of compressed air. Finally the residue was filtered on a Buchner funnel, and washed with sulphuric acid (6 N) until it no longer gave a spectroscopic test for germanium. The process of washing was slow and tedious, but was much prolonged by the simultaneous extraction of gallium<sup>2</sup>. These washings gave about one-half of the yield of germanium.

**Precipitation with Hydrogen Sulphide.**—The filtrates from the sulphuric acid extraction were placed in large glass cylinders, one-fifth volume of commercial sulphuric acid was added,

<sup>1</sup>It was found later that if the dish were heated just below boiling, the lead sulphate granulated and settled out, rendering filtration easy. For heating an asbestos collar resting on a tripod covered with gauze was used.

<sup>2</sup>A normal solution of sulphuric acid is recommended when germanium alone is to be extracted.

and the solution was allowed to stand over night to cool. Colorless crystals separated which, in the spectroscope, showed zinc only. To avoid this crystallization of zinc sulphate, 1 l. of water was added to each 10 l. of solution.

The solution was placed in 10 l. bottles and hydrogen sulphide was passed through it until most of the precipitate had settled out (at least an hour). After standing over night to complete the precipitation, the clear supernatant liquid was siphoned off. The precipitate was filtered on a Buchner funnel and washed with a solution of sulphuric acid (3 N) saturated with hydrogen sulphide.

**The Crude Sulphides.**—When sucked dry, this precipitate was readily removed from the paper by means of a porcelain spatula. The filter papers with the small amount of adhering precipitate were preserved for treatment to be described later. The precipitate was neutralized with ammonium hydroxide, evaporated to dryness, and ground to a fine powder. A spectroscopic test showed large amounts of zinc, cadmium, germanium and lead. Much arsenic was also present.

The washings from the sulphate residue were treated in a similar manner and yielded about an equal quantity of crude sulphides.

**Conversion to Crude Oxides.**—The dried sulphides were placed in a large evaporating dish and a small portion of nitric acid was added. The action was very vigorous and care was necessary to prevent loss by frothing. Further additions of nitric acid were made until violent action no longer occurred and the mass was covered with the acid. The dish was then gently heated and finally the solution was evaporated to dryness. Evaporation with nitric acid was repeated until oxidation appeared complete. The nitric acid was then driven off by heating until sulphur trioxide fumes appeared. If the mass were allowed to cool and solidify, a very hard enamel would be formed which could not be removed from the dish. This was avoided by stirring during the cooling which granulated the mass and rendered grinding easy. Some was also neutralized with ammonium hydroxide, evaporated to dryness and ignited to expel ammonium sulphate. This gave a powdery residue. About 870 g. of crude oxides was obtained. A spectroscopic test of the oxides from the washing of the sulphate residue showed large amounts of zinc, cadmium, and germanium and

a trace of gallium. Much arsenic was also present. These oxides were preserved for purification as described later.

The Filtrate from the Sulphide Precipitation.—After filtration of the sulphides, the filtrate soon became cloudy due to precipitated sulphur. These filtrates were stored in large glass cylinders. On standing several weeks the solution became clear while a white flocculent precipitate settled out. A spectroscopic test of this precipitate showed zinc, cadmium, and germanium, in moderate amounts. A portion of the solution, neutralized with ammonium hydroxide, evaporated and ignited to expel the ammonium sulphate, showed in the spectroscope zinc only. The solution was nearly saturated with zinc sulphate and other elements known to be present did not give a spectrum.

The Sulphide Filters.—These filters were collected in a bottle containing sodium hydrosulphide solution. After thus digesting several days, the solution was filtered on a Buchner funnel and the residue washed with sodium hydrosulphide solution<sup>1</sup>. The filter residue was burned in an iron dish and the ash added to the filtrate. After being digested for several days, with frequent stirring, the solution was again filtered. A spectroscopic test of the residue showed zinc, cadmium and lead, but no germanium.

The filtrate was subjected to Winkler's fractional precipitation method<sup>2</sup>. Three liters of solution were acidified with sulphuric acid so that it contained less than 10 cc. of six normal acid. The precipitate was immediately filtered and washed. Three such fractional precipitations, the second and third made with solutions even nearer the neutral point, gave arsenious sulphide precipitates containing considerable amounts of germanium sulphides, and filtrates in which germanium sulphide formed even while filtering. The latter was always distinctly tinged with yellow. The method gave only partial separations of arsenic and germanium. All precipitations were made in cold solutions.

<sup>1</sup>Prepared by saturating NaOH solution (3 N) with hydrogen sulphide until it gave a strong odor of the gas.

<sup>2</sup>J. Prakt. Chem. **142**, (1886) 193.

## PURIFICATION OF THE GERMANIUM

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The chemical behavior of arsenic and germanium are so similar that their separation is the most difficult problem in the purification of germanium. However, unexpected difficulty was encountered in the persistence of zinc in being carried down with germanium disulphide when a strongly acid solution containing these elements was saturated with hydrogen sulphide.

Winkler<sup>1</sup> purified germanium by a process of fractional precipitation. He made the sodium sulphide solution from argyrodite, already mentioned, just acid with sulphuric acid, thus precipitating arsenic and antimony as sulphide, and then recovered the germanium by precipitating it from the filtrate with hydrogen sulphide, after making the filtrate strongly acid with hydrochloric acid. Later<sup>2</sup> he recognized this product as impure and modified the process by precipitating with sulphuric acid, first from the slightly alkaline solution (antimony and most of the arsenic), then from a slightly acid solution (arsenic and germanium), and finally from the strongly acidified solution (most of the germanium). This product was still impure, and after oxidizing with nitric acid and igniting, the residue was further purified by dissolving in hydrofluoric acid and precipitating with potassium fluoride. The potassium fluogermanate was recrystallized. This certainly should have given a pure product.

Urbain, Blondel, and Obiedoff, working on zinc blendes, used a somewhat similar method of purification but introduced some new features. They extracted zinc from the sulphides by digesting with 15% sulphuric acid.

After repeated treatments with sodium sulphide and sulphuric acid, the sulphides were finally precipitated from a hydrochloric acid solution, redissolved in ammonium hydroxide, and the arsenic and traces of molybdenum separated from germanium by cautious fractional precipitation with hydrochloric acid. They say that perfectly white germanium sulphide was obtained from the solution.

The author found that precipitation in hydrochloric acid solution

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<sup>1</sup>J. prakt. Chem., **34** (1886) 193.

<sup>2</sup>J. Prakt. Chem., **36**, (1887) 183.

gave a purer product than that from sulphuric acid, also, that solution in ammonia gave a better separation than that in sodium sulphide. Nevertheless, he doubts the purity of the perfectly white sulphide.

Buchanan<sup>1</sup> obtained a nearly pure germanium solution by distilling the zinc oxide concentrates with hydrochloric acid in a current of chlorine. In small amounts he purified the product by precipitating with hydrogen sulphide, oxidizing the germanium disulphide with nitric acid, and preparing potassium fluogermanate from the residue. This should have given a pure compound of germanium.

Bardet<sup>2</sup> prepared germanium dioxide from the residue left after evaporation of certain mineral waters. His method was similar to Winkler's but he used magnesia mixture to precipitate the arsenic. He traced the action of germanium by means of the spectroscope.

The author found that magnesia mixture precipitates germanium almost completely so that it is likely much germanium was lost by this method of separation. The volatility of arsenic and magnesium in the precipitate would, undoubtedly, account for the failure of the spectroscope to detect germanium if present.

## EXPERIMENTAL

**Ignition of the Crude Sulphides.**—As both the oxides and sulphides of arsenic are very volatile while germanic sulphide is only slightly so, and is easily converted by ignition in air to the non-volatile germanic oxide, effort was made to separate these elements by ignition of their sulphides in a current of air, and later in a current of oxygen. The sample of crude sulphides used was the dried precipitate described under "Extraction of the Germanium." (p. 8.)

**Ignition of Crude Sulphides in a Current of Air.**—The sulphides, contained in a porcelain boat, were ignited in a hard glass tube, the heat being raised gradually to dull redness. A current of compressed air was passed through the tube and slowly bubbled through dilute sodium hydroxide solution.

The characteristic coatings for ignition of arsenious sulphide were obtained just beyond the boat. This sublimate rinsed into a dish and evaporated to dryness gave no test for germanium in the spectroscope.

Fumes were given off which were only partially absorbed by the

<sup>1</sup>J. Ind. Eng. Chem., **8**, (1916) 585.

<sup>2</sup>Compt. rend., **158**, (1914), 1279.

sodium hydroxide solution. They appeared to consist of volatilized sulphur. The sodium hydroxide solution was made six normal with sulphuric acid and saturated with hydrogen sulphide. A pale yellow precipitate was obtained which showed no germanium in the spectroscopic test.

The residue in the boat subjected to Marsh's test, using the silver nitrate modification, gave arsenic still present in abundance.

**Ignition of Pure Oxides of Arsenic and Germanium.**—In order to verify the above conclusion, and eliminate the effect of traces of other elements still remaining after the above purification, pure germanium dioxide and arsenious oxide were evaporated with nitric acid until the arsenic was converted to the pentavalent form, and then ignited in a porcelain dish to a red heat. A Marsh's test of the residue, using the silver nitrate modification, showed a large amount of arsenic still present, thus proving that arsenic is not separated by ignition with germanium even when other elements are completely excluded.

**Conclusions from Experiments on Ignition.**—Germanium is not appreciably volatilized by ignition in air even when in the form of germanium disulphide.

Arsenic is not expelled by ignition to redness when mixed with germanium, in the form of concentrates, of sulphides, oxides, or even of the pure oxides of the two elements with other bases absent. Ignition with an acid less volatile than the oxides of arsenic does not cause complete volatilization.

The fact that pure oxides of arsenic and germanium are not separated by ignition suggests the possibility of an arsenate or pyroarsenate of germanium, as the formation of a phosphate of germanium has already been noted<sup>1</sup>.

The partial separation of arsenic by volatilization of the oxides, as described above, appears to be a convenient method of preventing the accumulation of arsenic in by-products, thus making possible a practically complete separation of arsenic from germanium by the method of precipitation as potassium fluogermanate to be described later.

**Formation of Potassium Fluogermanate from Crude Oxides.**—The double salt potassium fluogermanate is easily formed, very crystalline, and much more soluble in hot than in cold water. It is, therefore, very suitable for purification by

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<sup>1</sup>Winkler, J. Prakt. Chem., **34**, (1886) 211.

crystallization as arsenic does not form such a double salt. These experiments were designed to effect a separation from accompanying elements by this method.

Commercial hydrofluoric acid was used in these preparations. Two determinations of the total acid present, by the method previously described, gave, respectively, 43.43% and 43.41% calculated as hydrofluoric acid.

Crystallized potassium fluoride was also used.

First Method.—In a large lead dish, 98.5 g. of crude oxides was treated with 149 g. of hydrofluoric acid (20%). The mixture was heated on a water bath to dissolve as much as possible of the white precipitate formed. The solution was filtered, and washed with hot water which dissolved any remaining white precipitate but left a gray insoluble residue.

Forty grams of potassium fluoride was added to the filtrate and the solution was evaporated to a volume of about 150 cc. The solution was allowed to stand over night when a mass of fine white crystals formed. These were filtered, washed with cold water, dilute alcohol (1:1), and 95% alcohol, then dried in the oven. The yield was 67.0 g. A spectroscopic test showed zinc, potassium, germanium, and a little gallium.

The filtrate was evaporated to one-third volume and set aside to crystallize. A mass of fine white crystals formed which were recrystallized as described later.

Second Method.—In a large lead dish 466 g. of crude oxides were treated with 346 g. of commercial hydrofluoric acid and 494 cc. of water (approximately 20% hydrofluoric acid). The mixture was stirred with a platinum spatula to effect solution as far as possible. Without filtering, a solution consisting of 330 g. potassium fluoride, dissolved in 1014 cc. of water, was added. This solution was evaporated to about 800 cc. and allowed to stand over night. A gray crystalline precipitate formed, which was filtered, washed with cold water, dilute alcohol (1:1), and 95% alcohol, and dried in the oven. The yield was 196.5 g. A spectroscopic test gave zinc, germanium, and potassium.

The filtrate was evaporated to a volume of 500 cc. and set aside to crystallize. It yielded a white crystalline product weighing 140 g. A spectroscopic test showed potassium, zinc, and cadmium, but no germanium.

The second filtrate was evaporated to 350 cc. It gave a similar product weighing 133.5 g. and showing in the spectroscope zinc and cadmium but no line of germanium.

The crude oxides treated by these two methods weighed 867 g. About 145 g. of the first product of crystallization was prepared by the first method and 250 g. by the second. Arsenic was not found by the spectroscopic tests, but was undoubtedly present in these products.

Recrystallization of the Potassium Fluogermanate.—The first product of crystallization by the second method was transferred to a three liter lead dish and extracted repeatedly by boiling with water. The solution from each extraction was decanted through a filter held in a rubber funnel. About 10 l. of solution was thus obtained. A gray residue was left on the filters which was preserved for further treatment.

The water extract was evaporated to about 6 l. in an 8 l. lead dish and allowed to crystallize over night. The crystals were filtered out, washed with cold water, and dried in the oven.

To the mother liquor, was added the first product of crystallization from the first method and the volume was made up to 8 l. The dish was heated over an asbestos collar supported on a wire gauze. Boiling was continued until solution was practically complete. The solution was evaporated to 6 l. and allowed to crystallize. The crystals were filtered, washed, and dried as before. The yield of the recrystallization was 151 g.

The product was again recrystallized. Fifteen grams was boiled with about 400 cc. of water in a platinum dish until the solution was saturated. The residue settled quickly and the supernatant liquid was decanted through a filter held in a rubber funnel. Extraction was repeated until the volume of the filtrate was about 600 cc. The

filtrate was received in a 700 cc. platinum dish. It was boiled down to a volume of 400 cc., using the free flame of a Bunsen burner. The solution was quickly cooled by placing the dish in cold water. This caused it to form a jelly-like mass. A little stirring would cause the jelly to disappear leaving a fine granular precipitate. Stirring, however, was not necessary.

After standing about three hours or over night, as was most convenient, the white finely crystalline mass was filtered, using paper held in a rubber funnel, and was washed twice with cold water. The process of crystallization was repeated by adding to the mother liquor enough of the product of the first recrystallization to saturate a volume of solution equal to the capacity of the dish, then boiling to effect solution, filtering, and extracting repeatedly with hot water until the dish was filled. The solution was then evaporated to saturation and treated as above described. When about 50 g. of crystals had been obtained, the mass was washed with cold water, dilute alcohol (1:1), and 95% alcohol, successively. All the product of the first crystallization was worked over in this way.

A dark gray residue was left on the filters. This was combined with the residue from the first crystallization. To this was added a solution, obtained by digesting with boiling water all the filters used in filtering the potassium fluogermanate. Extraction of the residue was then carried out as described above. It was continued to the first appearance of a white amorphous residue unlike the potassium fluogermanate. This was taken as indicating danger of contamination.

The portions of potassium fluogermanate thus obtained were dried in an electric oven for several days at  $108^{\circ}\text{C}$ ., thoroughly mixed and preserved as sample No. 2. The yield was 126 g. Proofs of the purity will be given under the analysis of potassium fluogermanate.

The gray residue still left on the filter was further extracted by boiling with water until very little solid separated on evaporating and cooling the extract. The residue was tested in the spectroscope and showed zinc, iron, calcium, and lead, but no germanium. Its weight was 30 g.

The hot water extract was evaporated to crystallization.

The crystals, filtered and washed with cold water, were combined with those obtained by evaporating to the point of saturation the mother liquor from the first recrystallization of the potassium fluogermanate.

This white crystalline mass was recrystallized by extraction with boiling water in the manner above described. Extraction was continued until jellying no longer took place on evaporating the solution and cooling. The crystals obtained were washed, dried and preserved as sample No. 3. The yield was 36 g.

A residue was left on the filter which showed in the spectroscopic calcium fluoride, and potassium, but no germanium.

## ANALYSIS OF POTASSIUM FLUOGERMANATE

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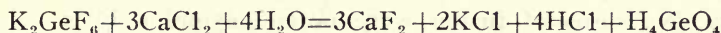
The purpose of this analysis was to establish its purity and thereby prove the accuracy of the method of purification. Serious difficulties were encountered at every hand because of the peculiar properties of germanium and its interference with established methods.

The samples have already been described. No. 1 was obtained from the germanium dioxide, prepared from the sulphide filters, and partially purified by Winkler's method of fractional purification. No. 2 was the main body of the double salt, prepared from the crude oxides, by the method described under "Purification of Germanium". (p. 15.)

Spectroscopic Tests and Solubility.—No. 1 gave on testing with the spectroscope only potassium and germanium. No. 2 gave by the same test potassium, germanium, and a possibility of a trace of calcium. As the carbons used in forming the arc contained small amounts of iron, sodium and calcium, the test was not conclusive for these elements. The calcium lines appeared to be enhanced by the presence of fluorine rendering the test for that element still more uncertain.

Both samples were soluble in 40 parts of boiling water having no detectable trace of solid. The solution appeared perfectly clear thus excluding more than a trace of calcium fluoride.

Test for Arsenic.—Twenty-five hundredths of a gram of Sample No. 2 was dissolved in 30 cc. of boiling water. Sodium carbonate solution was added until the solution was alkaline to litmus paper. Seven and one-half cc. of calcium chloride solution (1:10) was added. This caused the litmus paper to turn red. The precipitation of calcium fluoride causes a strong acid reaction, perhaps, according to the equation:



Sodium carbonate was added to a faint alkaline reaction. The solution was boiled, and allowed to stand on the hot plate until the precipitate settled. The precipitate was filtered and washed with hot water.

The precipitate was rinsed into a platinum dish and evaporated to dryness. The residue was moistened with water, 6 cc. of sul-

phuric acid was added, and the mass was evaporated to expel the hydrofluoric acid. Water was added and the solution was subjected to Marsh's test using the silver nitrate modification. Very little precipitation of silver occurred. The final test gave a slight precipitate resembling sulphur. It was filtered, washed, oxidized with potassium chlorate and hydrochloric acid, and subjected to Marsh's spot test. No trace of arsenic could be detected.

The filtrate was subjected to Marsh's test using the silver nitrate modification. A very slight precipitate, resembling sulphur, was obtained which was oxidized with potassium chlorate and hydrochloric acid, and subjected to Marsh's spot test. No trace of arsenic was found.

In each case the gas was passed through the silver nitrate solution for about one hour.

These tests assured a high grade of purity for the potassium fluogermanate, as the accompanying elements which were present in appreciable quantities in the original material were thus shown to be eliminated, and the process of preparation did not tend to accumulate traces of others.

Loss on ignition.—Krüss and Nilson<sup>1</sup> heated potassium fluogermanate in a covered crucible to beginning red heat. It lost 0.43% of "water of decrepitation." They state that it was then heated to a strong red heat for some time when it did not melt, but remained unchanged and showed no decrease in weight.

On the other hand, Winkler<sup>2</sup> gives a series of determinations showing losses ranging from 0.41% by heating one minute in a covered crucible at dark red heat to 29.017% on heating one hour at full red heat in an open crucible.

Direct Ignition.—Exactly one gram of sample No. 2 was weighed in a platinum crucible, covered, and ignited carefully at a dull red heat, the bottom of the crucible just showing the color. The crucible was cooled and weighed. The ignition was repeated but a constant weight was not obtained. A slight decrepitation was evidenced by the appearance of the salt. No signs of fusion were noted beyond a little cohesion of the salt. No evidence of volatilization or sublimation could be detected. The data are as follows:

<sup>1</sup>Ber., 20, (1887) 1698.

<sup>2</sup>J. prakt. Chem., 36, (1887) 202.

Weight of Crucible and $K_2GeF_6$ .....	21.4256 g.
Ditto, ignited 10 min. at dull red heat .....	21.4137 g.
Ditto, ignited again 10 min. at dull red heat ....	21.4011 g.
Ditto, ignited again 20 min. at dull red heat ....	21.3833 g.

Loss in weight ..... 0.0423 g.  
 Percentage of loss—4.23.

#### Ignition in a Snowdon Furnace<sup>1</sup>.

The furnace used was modified by using for the heating chamber a small porous cup wound with nichrome wire. The salt was weighed in a platinum crucible of such size that it rested in the porous cup with only a few millimeters of the rim protruding. The crucible was heated first in the electric oven, then in the air oven, and finally in the Snowdon Furnace. Regulation of the temperature was obtained by means of a bank of lamps connected to a 110 volt direct current circuit. The furnace was placed in series with the bank of lamps and was calibrated by means of a high temperature mercury thermometer. The temperature was increased by the addition of a lamp at a time to the circuit until the safe working capacity of the furnace had been reached. The data are as follows:

#### Loss on Ignition in a Snowdon Furnace.

Weight of Sample 2 of $K_2GeF_6$ .....	1.0000 g.
Weight of Platinum Crucible and Sample .....	21.4682 g.
Ditto, dried 2 hrs. in an electric oven at 112°C..	21.4682 g.
Loss .....	0.0000 g.
Dried in an air oven at 125-126°C.....	21.4682 g.
Loss .....	.0000 g.
Dried in an air oven at 156-160°C.....	21.4680 g.
Loss .....	.0002 g.
Heated in Snowdon Furnace (for 2. hrs.)	
at 190°C.....	21.4680 g.
Loss .....	.0000 g.
Ditto, at 262°C. (1 hr.) .....	21.4680 g.
Loss .....	.0000 g.
Ditto, at 338°C. (1 hr.) .....	21.4679 g.
Loss .....	.0001 g.
Total loss .....	.0003 gm.
Ditto, at 440°C., (50 minutes) .....	21.4679 g.
Loss .....	.0000 g.

<sup>1</sup>The Cornell Chemist, May, 1914.

### Determination of Water.

This was the first of the quantitative determinations made in order that the formula proportions might be used as a check upon other analyses and as a test of purity.

By Drying in an Electric Oven.—Five-tenths gram of Sample No. 1 was weighed in a small platinum dish and dried in the electric oven at  $110^{\circ}\text{C}$ . There was no loss in weight.

Five-tenths of a gram of Sample No. 2 was weighed in a platinum dish and dried in the same oven at  $105^{\circ}\text{C}$ . for one hour. The loss was 0.2 mg. The sample was dried for another day at  $105^{\circ}\text{C}$ .

Test in a Closed Tube.—Determinations of loss on ignition and fluorine having caused some doubt whether the composition of the potassium fluorgermanate was shown by the formula, a portion of the salt was ignited in a closed glass tube which had been tested to prove it free from water. Decrepitation began at once, at a dull red heat the mass fused, the glass was strongly etched, and water collected in the cooler part of the tube. As this "water of decrepitation," as Krüss and Nilson call it, could not be determined by the usual methods, absorption methods were used.

### By Ignition in an Electric Furnace and Absorption of the Liberated Fluoride by Passing Through Lead Oxide.

Apparatus:

Test tube for regulation of air pressure

Muencke gas wash bottle filled with  $\text{H}_2\text{SO}_4$

Schwartz tube filled with glacial phosphoric acid

Electric furnace with rheostat and hard glass tube

Two Schmitz tubes

U-tube filled with  $\text{CaCl}_2$  (safety)

Filter flask

Chapman air pump.

Test Tube. This was arranged to adjust the height of the water column. Excess of air pressure was used causing bubbling through the water. The height of the water column was set so that the sulphuric acid in the gas wash bottle was displaced almost to the opening. This assured constancy of pressure and a slight vacuum in the apparatus.

Combustion Tube. This was of hard glass and 24 in. long. Diameter  $\frac{3}{4}$  in. Rubber stoppers were used. The

column of litharge was 6 cm. long. A platinum boat was used.

Filter Flask. This was used to equalize any sudden change in the suction. Excess of suction was maintained with the air pump and the rate of bubbling was regulated by means of a screw clamp.

Rheostat. This consisted of a wooden frame on which were mounted strips of tin plate. By connecting this across the terminals of the direct current supply and attaching the apparatus as a shunt, a perfect control of the current up to 5 amperes was obtained.

Electric Furnace. This was a 9 in. section from a multiple unit electric furnace. It was calibrated by means of a thermocouple.

Preparation of Apparatus and Materials.

Schmitz Tubes. Two were used in series, both being weighed separately for each determination. They were first thoroughly washed with water and dried by rinsing with alcohol and passing air through them. They were finally dried in the electric oven. The glacial phosphoric acid was broken into coarse pieces and was held in place by perforated porcelain plates.

Hard Glass Tube. It was thoroughly washed, dried in a current of air, and finally dried by heating in the electric furnace for 3 hrs. with a current of dry air passing through it.

Litharge. As the supply on hand was not satisfactory, some was prepared by heating red lead ( $\text{Pb}_3\text{O}_4$ ) in a hard glass tube in the furnace for an hour at  $700^\circ\text{C}$ . The product was yellow when cold. It was tested<sup>1</sup> and found to contain a little chloride. This was washed out with boiling water. The litharge was dried by carefully heating in an iron pan over a triple burner.

Asbestos Plugs. These were ignited in a platinum crucible over a blast lamp. They turned brown.

Testing of Apparatus. After assembling, the apparatus was tested for leaks by causing it to support a column of water 15 cm. high for 10 min.

The apparatus was finally dried by running it as a blank determination. The empty end of the tube was heated

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<sup>1</sup>Krausch's Chemical Reagents, 3rd Ed. p. 159.

30 min. at red heat, then the furnace was moved to the litharge end which was heated for one hour at 500°C.

A blank determination was then run and the weight of the Schmitz tubes remained constant. In spite of these precautions, three determinations were run before the apparatus became constant.

Method. The boat was ignited, cooled in a desiccator, and weighed. One gram of Sample No. 2 of potassium flougermanate was weighed in the boat. The boat was placed in the combustion tube and a current of 4.5 amp. was passed through the furnace, thus heating the tube rapidly to the desired temperature. The current was then adjusted to maintain this temperature.

Compressed air was bubbled through the test tube and the height of the delivery tube was adjusted to give practically no column of sulphuric acid in the purifier to displace. The suction was started and the stop cocks in the Schmitz tubes were gradually opened until a gentle suction was obtained through the apparatus and a slow current of air was passing. Great care was necessary in opening the apparatus as either a back pressure or too rapid flow of gas would make refilling of the Schmitz tubes necessary. A little attention to the order of opening the stop cocks eliminated this danger.

The end of the tube containing the boat was heated for the chosen time, then the furnace was allowed to cool to the temperature chosen for heating the litharge end, and the furnace was gradually moved along to this end thus driving out any adhering moisture. After this heating, the furnace was cooled rapidly to about 100°C. when the stop cocks were closed in the Schmitz tubes and the apparatus disconnected.

The Schmitz tubes were handled with a dry cloth and were not wiped. They were allowed to stand near the balance case one-half hour and were opened for a moment before weighing to adjust the air pressure. All the apparatus was kept tightly stoppered while not in use.

Data:

- (a) Weight of Sample No. 2 of  $K_2GeF_6$ ....1.0000 g.  
Absorption of 1st Schmitz  
Tube ..... .0066 g.:  
Absorption of 2nd Schmitz : = 0.66%  
Tube ..... .0000 g.:  
Heated 3 hrs. at 500°C.  
Heated litharge end 1½ hrs. at 400°C.

The completeness of the dehydration was checked the next morning by heating for 30 minutes at 650°C., and holding the litharge end of the tube at 400°C. for one hour. The increase in weight of the Schmitz tube was 0.3 mg.

- (b) Weight of Sample No. 2 of  $K_2GeF_6$ ....1.0000 g.  
Absorption of 1st Schmitz  
Tube ..... .0063 g.:  
Absorption of 2nd Schmitz : = 0.67%  
Tube ..... .0004 g.:  
Heated 2 hrs. at 600°C.  
Litharge end at 400°C. for one hour.

The completeness of the dehydration was checked by heating the sample one-half hour at 600°C. and the litharge end at 400°C. for one hour. The increase in weight of the Schmitz tube was 0.1 mg.

The hard glass tube was strongly etched, showing decomposition took place. The bulb at the entrance of the Schmitz tube showed no sign of etching during these determinations.

The formula  $K_2GeF_6 \cdot 1/10 H_2O$  gives 0.676% water.

Determination of the Volatility of Potassium Fluogermanate on Evaporating a Water Solution.

This experiment was carried out as a check upon losses in the preparation of this salt, but the results are interesting when compared with those obtained from the water determination.

A sample of potassium fluogermanate weighing 0.5156 g. was weighed in a tared platinum dish and dried for 1 hr. on an air bath covered with asbestos paper. After weighing the dish and content, 60 cc. of water was added. The water was boiled until solution was complete. The solution was evaporated to dryness and the dish was heated as before for 1 hr. The weight of the dish and contents was exactly the same as before solution.

No volatilization of any constituent had occurred. Apparently decomposition did not occur. While the sample was not the same as that used in the water determinations, the mode of preparation was very similar and it undoubtedly contained water. That the water content after evaporation of the solution should be exactly the same as before appears remarkable, unless it be water of crystallization according to the formula given above.

Conclusions from determinations of water.

The potassium fluogermanate after thorough drying still contains some water which causes decrepitation when it is released.

The amount of water retained appears practically constant.

The water is given up by heating in a current of dry air at about 500°C.

On heating in a closed crucible the water is not given off appreciably until a temperature of over 500°C. is reached.

Decomposition begins in a current of dry air at about 500°C. At 600°C. the action is very marked. Both glass and quartz are strongly etched.

Ignition in a crucible at a dull red heat causes decomposition with no other evidence than a continued loss in weight.

The water in potassium fluogermanate cannot be determined by the usual method of drying in an oven as it is not released at such temperatures.

The water cannot be determined by the usual process of absorption with certainty as the temperature at which it is released lies too close to the temperature of decomposition.

The water can be determined accurately by the process of absorption if the gases are passed through pure lead oxide to absorb the liberated fluorides.

### **Evaporation of Potassium Fluogermanate with Sulphuric Acid.**

Krüss and Nilson<sup>1</sup> describe two analyses of potassium fluogermanate made by evaporating a solution of the salt in a platinum crucible with excess of sulphuric acid, first over a water bath, and finally at a higher heat. Adhering sulphuric acid was driven off by repeatedly heating with ammonium carbonate. The results show no appreciable loss indicating that germanium fluoride is not volatilized under such conditions.

On the other hand, Winkler<sup>2</sup> describes four experiments showing a loss of germanium by evaporation of the double fluoride, or

<sup>1</sup>Ber., 20, (1887) 1698.

<sup>2</sup>J. Prakt. Chem., 36, (1887) 196.

germanium dioxide and calcium fluoride, with sulphuric acid. In one instance he shows a loss of 5.42% of germanium dioxide by heating potassium fluogermanate with dilute sulphuric acid.

Evaporation in a Snowdon Furnace and Neutralization of the Sulphuric with Ammonium Carbonate or Hydroxide.

Five-tenths gram of Sample No. 2 was weighed in a platinum crucible, 10 cc. of water was added, and the mixture was heated in a Snowdon furnace. Dilute sulphuric acid in slight excess over the calculated amount was added, and the solution was evaporated at a temperature just below boiling until sulphuric anhydride fumes were given off. The temperature was gradually increased to the capacity of the furnace and continued until fumes were no longer expelled. After cooling, 2 cc. of ammonium carbonate solution (1:5) was added and the solution carefully evaporated to dryness. This treatment was repeated twice when the crucible was ignited and weighed. Evaporation with ammonium carbonate solution, ignition, and weighing were repeated but a constant weight could not be obtained. A flaky white residue remained which decrepitated so badly both on heating and on cooling the crucible that it was thrown out even when the crucible was covered.

Five determinations were made by this method varying the conditions to avoid the decrepitation. Two determinations were lost by creeping or spurling. In one ammonium hydroxide (1:1) was substituted for ammonium carbonate solution. None of these changes, however, gave constant results. A typical set of data is given below.

Weight of Sample No. 2 .....	0.5000 g.
Weight of crucible and residue evaporated three times with ammonium carbonate solution and ignited.....	19.1901 g.
Ditto, evaporated again with ammonium carbonate solution and ignited.....	19.1821 g.
Ditto, .....	19.1742 g.
Ditto, .....	19.1732 g.
Ditto, .....	19.1720 g.

Evaporation in a Snowdon Furnace and Neutralization with Ammonia Carried by a Current of Air.—

Current of Air.—This was modified from the device used by Kruss and Moraht<sup>1</sup>.

<sup>1</sup>Ann. c, 262 (1891) 51.

The sample was weighed in a platinum crucible. Fifteen cc. of sulphuric acid (1:6) was added and the mixture was heated in a Snowdon furnace. Solution was nearly or quite complete. The solution was evaporated at this temperature (no formation of bubbles was permitted). When about one-half of the liquid was gone, white crystals began to form and soon the solution was filled with the crystalline mass giving a jelly like consistency. A shell formed over the top interfering with the evaporation. Eight cc. more of sulphuric acid (1:6) was added. By means of a little agitation the solid was caused to settle to the bottom when evaporation readily occurred. The latter was continued until sulphur trioxide fumes were given off when the temperature was increased to the full capacity of the furnace and held there until no more fumes escaped.

After cooling the crucible was fitted with a perforated platinum cover bearing a bent glass tube held in place by a small bulb. Compressed air which was slowly bubbled through concentrated ammonium hydroxide solution was passed into the crucible. This was continued at room temperature  $3\frac{1}{2}$  to 4 hrs. A lamp bank was used to control the current as previously described. Two lamps (about  $190^{\circ}\text{C.}$ ) was first used. The temperature was gradually increased by adding a lamp to the circuit at intervals of  $\frac{1}{2}$  hr. until a temperature of about  $600^{\circ}$  was reached, the current of air saturated with ammonia being continued throughout the process. Heating was maintained at the full temperature from 2 to  $2\frac{1}{2}$  hrs. The crucible was then removed to a triangle covered as usual, and ignited first with a low flame and finally at a dull red heat for 15 minutes. It was then cooled and weighed. Treatment with ammonia was repeated for  $2\frac{1}{2}$  to 3 hrs. when the crucible was again ignited and weighed.

The residue was fairly tenacious and gave no decrepitation. No signs of loss were detected throughout the process.

Data:

(a) Weight of Sample No. 2 .....	0.5000 g.
Weight of platinum crucible and residue after 1st treatment with ammonia.....	19.1931 g.
Ditto, after 2nd treatment with ammonium .....	19.1931 g.
Weight of crucible .....	18.6704 g.
Weight of residue .....	.5227 g.

Calculation:

Percentage of  $K_2GeF_6$  in residue  
( $GeO_2 + K_2SO_4$ ) = 94.596

$$\frac{0.5227 \times 0.94596}{0.5000} = 99.27\% \text{ of } K_2GeF_6$$

(b) Weight of Sample No. 2.....	0.5000 g.
Weight of crucible and residue, 1st treatment .....	19.1940 g.
Weight of crucible and residue, 2nd treatment .....	19.1934 g.
Weight of crucible and residue, 3rd treatment .....	19.1938 g.
Weight of crucible .....	18.6702 g.

Weight of residue (2nd treatment)... .5232 g.

Percentage of  $K_2GeF_6$  = 99.36

Average, 99.32% of  $K_2GeF_6$

This gives for the percentage of water 0.68 which is an excellent agreement with that found.

### Determination of Germanium.

This was undertaken for the same purpose of proving the purity of the potassium fluogermanate. At the same time much information was obtained regarding the method of determining germanium by precipitation with hydrogen sulphide<sup>1</sup>.

Having proven that germanium is not volatilized by evaporation of potassium fluogermanate with dilute sulphuric acid, this method of decomposing the fluogermanate was utilized to determine the amount of germanium present.

<sup>1</sup>Winkler, J. prakt. Chem., 34, (1886), 228.

The method was as follows: Five-tenths gram of potassium fluogermanate was dissolved by boiling with 25 cc. of water in a platinum dish. Seven and one-half cc. of sulphuric acid (1:1) was then added, a few drops at a time, giving time for the escape of hydrofluoric acid. During this addition the dish was heated on an air bath. The solution was not allowed to boil. A test by etching showed that hydrofluoric acid was being given off. The solution was then evaporated to about one-half volume. A small amount of granular white powder separated.

The solution and precipitate were transferred to a 500 cc. Erlenmeyer flask with water. The solution was made approximately 1:6 with sulphuric acid, cooled, and saturated with hydrogen sulphide, the gas being passed for about an hour. The flask was stoppered and allowed to stand over night.

The precipitate was filtered, washed with sulphuric acid (1:13) which had been saturated with hydrogen sulphide. It was then rinsed into a No. 6 porcelain crucible. The filter was washed four times with ammonium hydroxide by dripping it over the paper. The paper was burned in a separate crucible, taking care that the ash did not stick to the porcelain. The ash was then added to the remainder of the precipitate. The solution in the crucible was evaporated to dryness over a hot plate and concentrated nitric acid was added to convert the residue to germanium dioxide. Action here was too violent. Nitric acid (1:1) is better. The acid was evaporated off and the treatment was repeated.

Ammonium hydroxide was added to neutralize adhering sulphuric acid. It was evaporated off and the residue was ignited and weighed as germanium dioxide. Percentage of germanium in germanium dioxide—69.38.

The evaporation to dryness in the crucible required much care because of danger of loss by spurting. Two determinations gave low results because of this. The filtrates from these two determinations were combined, saturated with hydrogen sulphide, and allowed to stand several days. A white flocculent precipitate settled out which was filtered, washed, oxidized with nitric acid, and tested in the spectroscope. It gave a strong test for germanium.

Corrections were, therefore, made on the filtrates from the last two determinations in a similar manner. The precipitates

were subjected to the same treatment as the main body of the germanium disulphide. The results were as follows:

Number	Weight of Sample	Percentage of Germanium in First Precipitate	Correction Weight of $\text{GeO}_2$	Corrected Percentage of Germanium
1	0.5000	27.04	.....	.....
2	1.0000	26.90	0.0042	27.20
3	1.0000	26.88	0.0036	27.13

The percentage of germanium present calculated from the formula allowing for the water present as shown by the average of the best determinations was 27.21. That given by calculation from the residue after evaporation with sulphuric acid was 27.20.

Conclusions from the Results of the Analysis of Potassium Fluogermanate.—The main purpose of this analysis, the proof of the purity of the potassium fluogermanate and the consequent verifications of the method of extraction and purification is well established by: first, spectroscopic test together with the absense of arsenic and the solubility of the salt; second, agreement between the determination of water, the evaporation with sulphuric acid, and the direct determination of germanium.

Other important facts established are as follows:

Separation of arsenic and germanium can be accomplished by formation of potassium fluogermanate and two recrystallizations.

Water remains in the salt after drying for several days at 105-110°C. The water is not driven off at temperatures below 500°C.

A method for the accurate determination of water in potassium fluogermanate.

The constancy of the salt on evaporation with water, both regarding volatility of its constituents and the amount of water present.

Decomposition of the salt at a dull red heat and the temperature at which it begins to decompose when heated in air.

Temperature at which decomposition begins when heated in a current of dry air. The amount of germanium volatilized is a considerable portion of that present.

Germanium is not volatilized by evaporation of potassium fluogermanate with dilute sulphuric acid.

A method for testing the purity of potassium fluogermanate by evaporation with sulphuric acid and of neutralizing the sulphuric acid adhering, without the usual mechanical loss.

The determination of potassium by either the perchlorate or the chlorplatinat methods gives erroneous results due to the contamination with germanium dioxide.

The determination of fluorine by precipitation as calcium fluoride does not give accurate results, apparently due to the interference of germanium.

A direct method of determining germanium in potassium fluogermanate.

The incomplete precipitation of germanium by saturation of the acid solution with hydrogen sulphide and a method of correcting for the same.

## DETECTION OF GERMANIUM.

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Th. Richter seems to have been the first to subject this element to a blow pipe analysis but apparently did not suspect its presence. Later Penfield<sup>1</sup> detected germanium in argyrodite from a new source by this means.

The method most frequently employed for the detection and identification of germanium has been the formation of some of its principal compounds, such as the sulphides, sulphogermanates, and fluogermanate, also, the element itself.

The spectroscope, with either the arc or spark spectrum, was employed for the detection of the element in new sources by Urbain<sup>2</sup>, Bardet<sup>3</sup>, and Dr. Burns of the U. S. Bureau of Standards<sup>4</sup>.

Buchanan<sup>5</sup> distilled the material with hydrochloric acid in a current of chlorine gas and identified germanium by precipitation of the white sulphide and by preparation of the fluogermanate.

Browning and Scott<sup>6</sup> modified the method by using instead of chlorine gas an oxidizing agent such as potassium chlorate, manganese dioxide, potassium permanganate, or potassium dichromate. They relied upon the precipitation of the white sulphide with hydrogen sulphide for identification of the element.

The author has not been able to tell with certainty the presence of a small amount of germanium in a solution containing chlorine by means of the precipitation with hydrogen sulphide, on account of the simultaneous precipitation of sulphur. Even in hydrochloric acid solution with no chlorine present precipitates were obtained which certainly appeared to contain germanium disulphide, but which, on oxidizing with nitric acid and igniting, gave no appreciable residue.

### Spectroscopic Test.

Of all the methods used for the detection of germanium, that with the spectroscope, as described below, proved the most reliable. It was used throughout the work to trace the presence of the element in the products obtained. Over 300 samples were thus tested.

<sup>1</sup>Am. J. Sci., (3) 40, (1893) 107.

<sup>2</sup>Compt. rend., 149, (1909) 602.

<sup>3</sup>Compt. rend., 157, (1913) 225.

<sup>4</sup>J. Ind. Eng. Chem., 8, (1916) 225.

<sup>5</sup>J. Ind. Eng. Chem., 8 (1916), 586.

<sup>6</sup>Am. J. Sci., 44, (1917) 313: 46, (1918) 663.

The method was as follows: an electric arc was prepared from ordinary electric light carbons using about one-quarter of a carbon for each electrode. The sample, in the form of a dry powder, was placed on the lower (positive) carbon. The length of exposure was controlled by a switch.

A Hilger spectroscope with fixed collimator and telescope was used, also a photographic attachment.

Exposure was made for about three seconds, the time depending upon the volatility of the elements present. Readings were made directly from the negative by Mr. R. W. G. Wyckoff. The arc always contained iron, calcium, and sodium, generally also barium, but these did not interfere in most of the tests. A comparison of the intensity of these lines with those from the sample was often made by taking a photograph of the arc itself. As a glass prism was used only the lines in the visible spectrum were obtained. In fact, only one line was prominent enough to be of service. This line is of slightly greater wave length than the third of the zinc triplet (4680.4 A. U.) It practically coincides with the edge of fourth band for carbon in the blue (about 4684. A. U.)

The test was found to have certain limitations. Positive results were very certain but negative results and evidence of traces were often unreliable. The latter was mainly due to the coincidence of the principal germanium line with a carbon band.

In general, volatile substances often caused failure, probably by cooling the arc below the point where germanium is volatilized. This was partially overcome by lengthening the time of exposure. It was often possible to drive off the volatile compound by ignition. The elements which caused this effect were arsenic, silver, magnesium, molybdenum, and potassium. Ammonium hydroxide was first used for neutralizing the sulphuric acid adhering to the sulphide precipitate. It was found to enhance the carbon band, which coincides with the germanium line, rendering the readings unreliable for small amounts of germanium. Sodium hydroxide was tried but the spectrum was so brilliant that it covered the germanium line. Potassium hydroxide was then used but apparently suppressed the line by its volatility. The sulphides, especially, when much arsenic was present, gave a similar effect. This was largely obviated by oxidizing the sulphides with nitric acid and igniting. In some cases adhering sulphuric acid was neutralized with ammonium hydroxide, evaporated and the residue ignited. This prevented the effect of the ammonium salt.

Lead, zinc, cadmium, tin, copper, and barium, in the amounts usually found, caused no interference. However, residues obtained by evaporation of solutions containing large amounts of any of these salts usually failed to give the germanium line, even when an appreciable quantity of the element was present.

When the calcium compound was the main constituent present, the spectrum gave a line which could not be readily distinguished from that of germanium.

**The Molybdate Test.**—To determine whether germanium would interfere with this test, pure germanium materials were used, following the directions given in Dennis and Whittelsey's *Qualitative Analysis*, page 33.

Germanium dioxide, from a quantitative determination of germanium in pure potassium fluorogermanate, was dissolved by boiling with water until the saturated solution was obtained. This solution was filtered, acidified with nitric acid, and added to a solution of ammonium molybdate. The mixture was warmed on a water bath to 70°C. A copious yellow precipitate resulted, indistinguishable from that given by arsenic.

Pure germanium dioxide was boiled with potassium hydroxide solution (1:10). The solution was filtered, acidified with nitric acid, and tested as above described. A copious yellow precipitate of similar appearance resulted.

The conclusions from these experiments were, that germanium under similar conditions forms a compound with ammonium molybdate that cannot easily be distinguished from that given by arsenic and phosphorus. In these materials, phosphoric acid was excluded by the method of preparation, and arsenic had been repeatedly proven absent.

The spectroscopic test is useless in the presence of molybdenum.

The molybdate test evidently cannot be used in the presence of germanium as a test for arsenic.

It appeared promising as a test for germanium when arsenic was excluded, as in the distillation method, or perhaps on the precipitate from the reduction of germanium with zinc and sulphuric acid.

## PREPARATION OF PURE GERMANIUM DIOXIDE.

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Germanium dioxide proved to be the most convenient starting point for much of the study of the chemistry of germanium, especially from the analytical view point. Its preparation in a high state of purity is, therefore, important.

Winkler<sup>1</sup> recommends hydrolysis of the chloride as giving the purest product but states that the yield is not good. He also mentions its preparation by ignition of the element in oxygen by roasting germanium disulphide and by heating the latter with sulphuric acid.

Preparation from Potassium Fluogermanate.

Evaporation with Sulphuric Acid and Precipitation with Hydrogen Sulphide.—It was desired to obtain germanium dioxide from the potassium fluogermanate already prepared whose purity had been established.

Winkler states<sup>2</sup> that potassium fluogermanate can be decomposed and the fluorine eliminated by evaporation with sulphuric acid but the procedure for large quantities is not to be recommended because of volatilization of germanium fluoride.

Since the author had proven that evaporation of this double salt with dilute sulphuric acid leads to no loss of germanium, the method was tried for preparation of pure germanium dioxide.

Sixteen grams of potassium fluogermanate was dissolved by boiling it with 700 cc. of water in a platinum dish. To this was slowly added 60 cc. of sulphuric acid (1:1). The mixture was evaporated to one-half its volume. It was transferred to a 2 l. Erlenmeyer flask with water and made up to a volume of 1540 cc. Five hundred and sixty cc. of sulphuric acid (1:1) was added, giving 2100 cc. of solution with a concentration of acid of 1:6.

Hydrogen sulphide was passed from the Kipp's generator until precipitation appeared complete. The flask was stoppered and allowed to stand over night. The precipitate was fil-

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<sup>1</sup>J. prakt. Chem., **34**, (1886) 211.

<sup>2</sup>J. prakt. Chem., **36**, (1887) 186.

tered and washed with sulphuric acid (1:9) which had been saturated with hydrogen sulphide.

The sulphide was rinsed into a weighed porcelain evaporating dish and the adhering precipitate was dissolved with ammonium hydroxide (1:1). The solution was evaporated to one-half volume, nitric acid (1:1) was added, and evaporated off. Treatment with nitric acid (concentrated) was repeated until oxidation appeared complete. The residue was then evaporated with ammonium hydroxide, ignited, and weighed. Treatment with ammonium hydroxide was repeated. A correction for solubility of germanium disulphide was made as usual.

Data:

Weight of  $\text{GeO}_2$  in the  $\text{K}_2\text{GeF}_6$  ..... 6.275 g.

Weight of  $\text{GeO}_2$  found ..... 6.060 g.

A slight spattering occurred which would account for part or all of the difference. The result shows that in as large quantities as could be handled the loss by volatilization is inappreciable, and probably practically none occurs. Several other such preparations pointed to the same conclusion but the data were not so definite. Attention should be called to the fact that the conditions for evaporation were a dilute solution and an addition of sulphuric acid, a few drops at a time.

## THE DETERMINATION OF GERMANIUM

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No satisfactory method for the separation of germanium from the accompanying elements and determination of the germanium has yet been described. Winkler<sup>1</sup> used a method of determination of germanium in the argyrodite ore based on the separation with sodium sulphide and separation of arsenic by fractional precipitation, finally precipitating the germanium as the disulphide and converting the latter to dioxide. The results could be only approximate.

Penfield determined germanium in argyrodite<sup>2</sup> and later in canfieldite<sup>3</sup> by decomposing the mineral with nitric acid, separating the silver with ammonium thiocyanate, and after a further purification with ammonium sulphide, obtained the germanium as the dioxide by evaporating the solution with nitric acid. Arsenic appears to have been absent.

The methods here described were based on that proposed by Winkler of precipitating germanium as germanium disulphide and converting to the dioxide, the conditions for which, however, had not been well described.

### Determination of Germanium in Pure Solutions.

**Solution of Germanium Dioxide in Water.**—Two and one-half grams of pure germanium dioxide was boiled with 2 l. of water for about 2 hours. The solution was filtered twice but was still slightly turbid. On standing 2 days, a slight amount of solid settled out. Four cc. of ammonium hydroxide was added but the solution was still turbid. Eight cc. of nitric acid was added and the solution was again boiled. This gave a clear solution which was permanent until completely used.

The solution was standardized by evaporating 50 cc. in a platinum dish over a water bath, igniting the residue over a triple burner, cooling in a desiccator, and weighing. The results were as follows:

50 cc. Germanium Dioxide Solution = .0618 g.  $\text{GeO}_2$

50 cc. Germanium Dioxide Solution = .0614 g.  $\text{GeO}_2$

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<sup>1</sup>J. prakt. Chem., 34 (1886) 228.

<sup>2</sup>Am. J. Sci., (3) 46, (1893) 110.

<sup>3</sup>Am. J. Sci., (3) 47, (1894) 452.

A second solution was prepared in a similar manner using 3 g. germanium dioxide, 2 l. of water, 5cc. ammonium hydroxide, and 8 cc. nitric acid. In standardizing the solution, it was found that great care was necessary in handling the ignited residue as it was easily lost in slight currents of air. Two determinations were lost through the rush of air on opening the desiccator. By covering the dish with a watch glass and carefully opening the desiccator, this was avoided and very constant results were obtained. Four determinations were as follows:

40 cc. Germanium Dioxide Solution gave 0.0588 g.  $\text{GeO}_2$   
40 cc. Germanium Dioxide Solution gave 0.0588 g.  $\text{GeO}_2$   
40 cc. Germanium Dioxide Solution gave 0.0588 g.  $\text{GeO}_2$   
40 cc. Germanium Dioxide Solution gave 0.0587 g.  $\text{GeO}_2$

#### A Study of Conditions for the Determination of Germanium by Precipitation as Germanium Disulphide.

(1). In Sulphuric Acid Solution.—Method. An acid solution of germanium dioxide was prepared having a volume of about 150 cc. and the proportions indicated below. The solution cooled to room temperature was treated in an Erlenmeyer flask with hydrogen sulphide, the gas being passed from 45 min. to 1 hr., and until most of the germanium disulphide had settled out. The flask was stoppered and allowed to stand over night. The precipitate was filtered and washed as indicated below. The treatment of this precipitate was so varied that each case will be described separately, but in all cases it was converted to the dioxide, adhering sulphuric acid was removed by use of ammonium hydroxide or carbonate, and the residue was weighed as germanium dioxide.

The filtrate from germanium disulphide had been shown to contain germanium. It was saturated with hydrogen sulphide and the flask was allowed to stand, stoppered, for at least two days, when a nearly white precipitate settled out. This was filtered, washed, converted to the dioxide, and weighed. The results were as follows:

Data :

# Determinations of Germanium in Pure Solutions.

No.	GeO <sub>2</sub> Present grams	Ratio H <sub>2</sub> SO <sub>4</sub> to other liquids by volume	Per cent alcohol by weight	Washed with		Weight of GeO <sub>2</sub> found		
				Acid solution	Alcohol	First pre- cipitate gr.	Correction gr.	Total gr.
1.....	0.1492	1:10	None.....	H <sub>2</sub> SO <sub>4</sub> (1:13). +H <sub>2</sub> S	None.....	0.1231	.....	.....
2.....	0.1492	1:6	None.....	H <sub>2</sub> SO <sub>4</sub> (1:13). +H <sub>2</sub> S	Until free from SO <sub>4</sub>	0.1475	0.0018	.1492
3.....	0.1492	1:6	"	"	"	0.1503	.....	.....
4.....	0.0616	1:6	"	H <sub>2</sub> SO <sub>4</sub> (1:9). +H <sub>2</sub> S	"	0.0602	0.0013	0.0615
5.....	0.0616	1:6	"	"	"	0.0600	0.0009	0.0609
6.....	0.0616	1:6	"	"	25cc.....	0.0592	.....	.....
7.....	0.0616	1:6	"	"	100cc.....	0.0576	Volatili zed.	.....
8.....	0.0616	1:6	"	"	300cc.....	0.0601	Volatili zed.	.....
9.....	0.0616	1:6	"	Washing solu- tion.	Until H <sub>2</sub> SO <sub>4</sub> was gone.	.....	.....	0.0620
10.....	0.0616	1:6	14.9	"	25cc.....	0.0602	0.0016	0.0618
11.....	0.0616	1:6	14.9	"	"	0.0589	0.0015	0.0604
12.....	0.0616	1:6	14.9	"	"	0.0600	0.0008	0.0608
13.....	0.0616	1:8.8	19.8	"	"	0.0595	0.0016	0.0611
14.....	0.0616	1:11.6	25	"	"	0.0573	0.0032	0.0605

## Explanations :

No. 1. This experiment was made to determine whether a more dilute sulphuric acid solution would give a more or less complete precipitation of germanium. The precipitate was rinsed into a No. 6 porcelain crucible with a jet of water. Ammonium hydroxide (1:1) was dripped over the filter (about 5 cc.). The filter was burned separately and the ash added to the main precipitate. The contents of the crucible was evaporated to one-half volume over an air bath. Five cc. HNO<sub>3</sub> (1:1) was added and evaporation was continued nearly to dryness. Five cc. of concentrated nitric acid was then added and the solution was again evaporated to dryness. The residue was ignited over a Bunsen burner. Ammonium hydroxide was added and evaporated off. The crucible was again ignited and weighed. Treatment with ammonium hydroxide and ignition were repeated to constant weight. The result shows a very incomplete precipitation in sulphuric acid solution of concentraton 1:10.

No. 2. This differed from No. 1 in that the precipitate after the washing with sulphuric acid solution was washed with alcohol

until free from sulphuric acid. The purpose was to prevent charring when the precipitate was dried so that it could be removed from the filter and the latter burned separately. The precipitate was evaporated with nitric acid in a No. 00 porcelain dish and the moist residue was transferred to a No. 7 porcelain crucible. The procedure in No. 1 was better in this respect.

No. 3. The precipitate and filter were transferred to a No. 6 porcelain crucible and 5 cc. of nitric acid (1:1) was added. The solution was evaporated to dryness, which oxidized the germanium disulphide and disintegrated the filter. Nitric acid was again added and evaporated off. The carbonaceous matter was burned off in the open crucible. The residue was again treated with nitric acid, evaporated, ignited, and weighed. The residue was treated with ammonium hydroxide and ignited, as described above, to a constant weight. In spite of the constant weight indicating no sulphuric acid present the result was high. Two out of three other determinations by this treatment of the precipitate gave high results.

Nos. 4 and 5 were a test of the direct ignition of filter and precipitate. The wet filter was transferred to a No. 7 porcelain crucible and dried over a low flame with the cover on. The cover was removed and the filter burned using about a half flame of a Bunsen burner. A hard black mass resulted which was crushed in the crucible with a glass rod, and then ignited until white. No. 5 did not burn white and was, therefore, evaporated with concentrated nitric acid after which a white residue was easily obtained. Ammonium hydroxide was added, evaporated, and the crucible was again ignited. A constant weight was readily obtained. The correction was made by burning filter and precipitate in the crucible, with the main body of germanium dioxide.

Nos. 6, 7, and 8 were made to test the use of alcohol for removing sulphuric acid from filter and precipitate. The purpose in the use of alcohol was to enable the drying of the precipitate so that it could be removed from the filter and the latter burned separately.

The filter and precipitate were dried in the electric oven. The precipitate was removed to a watch glass by means of a camel's hair brush. The dry germanium disulphide adhered to the brush badly so that mechanical loss probably occurred in the first two determinations. In No. 6 the filter slightly charred and was brittle. The other two were unsatisfactory.

The corrections were made by treating the precipitate in the

same way as the main portion, but the filter was burned in the same crucible with the germanium dioxide previously formed. The crucible was covered during the drying and the cover was left on too long resulting in volatilization. In No. 6 the crucible cracked giving an uncertain result.

No. 9 was a test of the utility of a washing solution which had been used for lead sulphate. After washing the precipitate with this solution it was washed with alcohol until the washings gave no test with barium chloride. The precipitates from the first precipitation and the correction were treated together by the method described under No. 1. Ammonium carbonate was used instead of ammonium hydroxide for removing adhering sulphuric acid.

The washing solution consisted of 740 cc. of water, 250 cc. alcohol, and 10 cc. sulphuric acid. In later experiments this solution was saturated with hydrogen sulphide and filtered. A test of the solubility of germanium disulphide in this solution was made by mixing the two in an Erlenmeyer flask, with frequent shaking during a period of several hours, and then allowing the flask to stand stoppered over night. The solution was filtered until clear. One hundred cc. of the filtrate was evaporated in a platinum dish over a water bath and the sulphuric acid was expelled by heating over an air bath. The dish was then ignited and weighed. The residue was evaporated with hydrochloric and sulphuric acids, and the dish again ignited and weighed. This was repeated until a constant weight was obtained. No loss in weight was detected by the evaporation with hydrochloric acid, showing no appreciable solution of germanium disulphide in the washing solution.

Nos. 10, 11, 12, 13, and 14 were a study of the completeness of the precipitation of germanium disulphide in solutions containing alcohol, in an effort to avoid the necessity for making the correction. The method varied from No. 9 only in using the washing solution saturated with hydrogen sulphide and in the treatment of the precipitate. In No. 10 the precipitate was dried and separated from the filter. In No. 12 the wet filter was burned directly. In Nos. 11, 13, and 14 the precipitate was rinsed into a No. 00 porcelain evaporating dish with ammonium hydroxide (1:1). The solution was evaporated to one-half volume, 5 cc. of nitric acid (1:1) was added, and evaporation continued to moist dryness. A little hot water was added and the contents of the dish were transferred to a No. 7 porcelain crucible. The solution was evaporated to dryness and

the crucible was ignited and weighed. Dry ammonium carbonate was added and the crucible was ignited and weighed.

The filtrates in the last five determinations were clear until the alcohol was added, when a fine white precipitate, like that of precipitated sulphur formed. In order to determine whether this was due to dissolved germanium disulphide, the precipitate from the five determinations, were filtered on the same filter, washed with washing solution and ignited directly. The weight obtained was 0.2 mg. which was no more than that given by blank determinations of the filter paper.

**CONCLUSIONS.** A sulphuric acid solution of concentration 1:10 gives incomplete precipitation of germanium disulphide. With a concentration of 1:6, it is nearly complete but a correction is necessary.

Alcohol in the solution in which germanium disulphide is precipitated does not avoid the correction. It seems to make the precipitation a little more complete, but the effect is not sufficient to warrant its use. As alcohol is increased and sulphuric acid decreased precipitation is less complete.

Alcohol can be used to wash out the sulphuric acid from the precipitate as it does not dissolve germanium disulphide appreciably. The precipitate and filter can then be dried in an oven without charring the latter.

The washing solution above described appears very satisfactory for washing the precipitate. It is doubtful whether saturation with hydrogen sulphide is necessary. If not, it would be more pleasant to use.

The precipitate after washing with alcohol and drying can be transferred to a watch glass and the filter burned separately. The procedure is somewhat objectionable on account of the powdery character of dried germanium disulphide. Nevertheless, it is more simple than Winkler's method of handling the precipitate and gives as accurate results.

Evaporation of filter and precipitate with nitric acid and ignition of the residue seems to lead to high results for an unknown reason. The procedure possesses little advantage and is not to be recommended.

Direct ignition of the wet filter gives good results and is by far the simplest method. An open crucible must, however, be used.

**The Final Method.**

The method as finally worked out is as follows: the germanium

solution, contained in a 500 cc. Erlenmeyer flask, is made up to a volume of 175 cc. with a concentration of sulphuric acid of 1:6. A rapid stream of hydrogen sulphide is passed through the solution for at least 45 min. and until most of the germanium disulphide has settled out. The flask is stoppered and allowed to stand overnight. The precipitate is filtered and washed with washing solution (740 cc. water, 250 cc. alcohol, 10 cc. sulphuric acid, saturated with hydrogen sulphide). The filter with precipitate is transferred to a No. 7 porcelain crucible, dried, and then charred over a low flame (the cover having been removed) until a small black mass is obtained, or, when only a small amount of germanium is present, until the carbon is burned off. Nitric acid is added and the crucible is covered with a small watch glass. The crucible is heated gently until violent action is over when the watch glass is removed, rinsed with a little nitric acid, and the contents of the crucible are evaporated to dryness. The residue is crushed by means of a glass rod as soon as the crucible is cooled. It is then ignited over a Bunsen flame until white, cooled, and weighed. Ammonium carbonate is added and the crucible is ignited gently with the cover on. When the ammonium carbonate is gone the crucible is again ignited and weighed. The treatment is repeated until a constant weight is obtained.

A correction for the solubility of germanium disulphide in the filtrate is necessary. It is made by saturating the filtrate contained in an Erlenmeyer flask with hydrogen sulphide, stoppering the flask, and allowing it to stand at least two days. A white precipitate composed largely of sulphur settles out. This is filtered and treated as described above. Both the main precipitate and the correction may conveniently be treated together in the same crucible, thus avoiding several operations.

In precipitating germanium disulphide, it is probable that the volume can vary through rather wide limits, but the concentration of the acid cannot vary much from that used.

A rapid and continuous stream of hydrogen sulphide seems to be necessary. A few times when the generator worked badly and the current was intermittent, the precipitation was incomplete.

In igniting the precipitate and filter, volatilization seems to occur if the cover is left on the crucible, as a low result is obtained and a black sublimate forms on the cover and sides of the crucible which does not burn off readily. The composition of this sublimate is uncertain as it does not burn white as readily as would germanium.

In an open crucible no evidence of volatilization is detected. The filter chars to a hard black mass when much germanium is present. The mass is rather difficult to crush with a glass rod without loss and burns white very slowly. After treatment with nitric acid, the residue is easily crushed and quickly burns white. If crushed immediately after drying it does not stick to a glass rod or brush but it is hygroscopic and causes trouble if allowed to stand. Care should be exercised that all of the carbon is burned off as it may, if present, cause loss by volatilization. If its presence is suspected the treatment with nitric acid and ignition in an open crucible should be repeated.

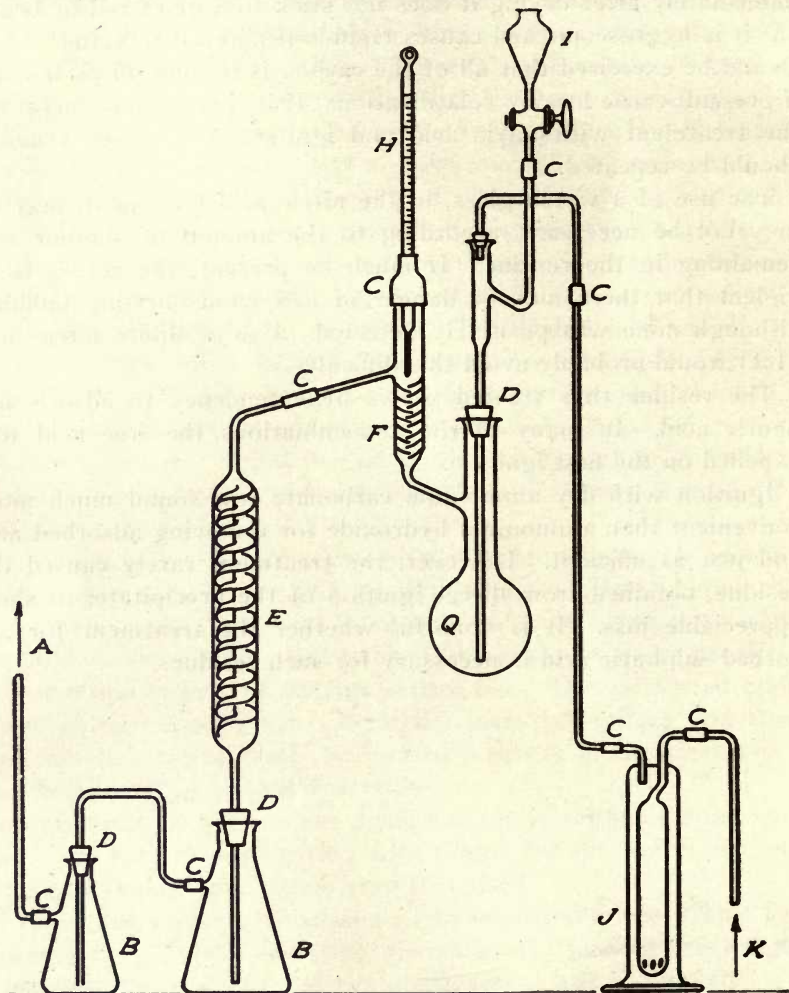
The use of a watch glass, in the nitric acid treatment, may or may not be necessary, according to the amount of sulphur still remaining in the residue. If much be present, the action is so violent that there may be danger of loss from bursting bubbles, although none was positively detected. Use of dilute nitric acid (1:1) would probably avoid this difficulty.

The residue thus treated shows little tendency to adsorb sulphuric acid. In many of the determinations the free acid was expelled on the first ignition.

Ignition with dry ammonium carbonate was found much more convenient than ammonium hydroxide for removing adsorbed acid and just as efficient. However, the treatment rarely caused the residue, obtained from direct ignition of the precipitate, to show appreciable loss. It is doubtful whether the treatment for adsorbed sulphuric acid is necessary for such residues.

# DETERMINATION OF GERMANIUM IN THE GERMANIUM CONCENTRATES

The apparatus used is shown in the figure:



- A. Connection to hood.
- B. Filter flasks containing 100 cc. water. The flask was cooled in ice water.
- C. Rubber connections.
- D. Corks.
- E. Spiral condenser.
- F. Vigreux tube sealed to distilling flask.
- G. Distilling flask.
- H. Thermometer.
- I. Separatory funnel.
- J. Muencke gas wash bottle.
- K. Current of chlorine gas from a cylinder.

Method. Twenty grams of germanium concentrates was weighed in a small crystallizing dish and transferred to the distilling flask using a short stemmed funnel and a platinum rod. Fifty cc. of a solution containing 5 g. of potassium hydroxide was poured through the funnel washing down part of the adhering powder.

The distilling flask was replaced in the apparatus and a stream of chlorine gas was bubbled through the solution. The flask was heated over an air bath. Chlorination was continued until the temperature rose nearly to the boiling point, the flask being shaken occasionally to secure complete oxidation. The color of the mixture changed to a chocolate. About 20 min. were required for the chlorination.

The dish in which the concentrates were weighed, the platinum wire, and the funnel were rinsed with 80 cc. of hydrochloric acid. The acid was then added to the separatory funnel of the apparatus and run in a slow stream into the distilling flask, care being taken that the evolution of gas was not so rapid as to endanger complete absorption of the germanium chloride in the receiving flask. About 10 min. were used for this addition. The burner was removed during this process but the chlorine was not interrupted.

Heating was continued over the air bath until the contents of the flask boiled vigorously, then over a wire gauze covered with asbestos paper. Distillation was continued until the volume was reduced to the original volume of the potassium hydroxide solution. The burner was removed, the chlorine delivery tube disconnected and the receiving flask replaced by a similar one. The first flask was labelled "Distillate I".

The chlorine was again passed. Fifty cc. of hydrochloric acid was added to the distilling flask and the solution was again distilled to the original volume. This process was repeated. The second receiving flask was labeled Distillate II; the third, Distillate III; the small flask, used to catch any germanium chloride that might be carried over from the receiving flask, was labelled "Safety Flask." To the latter was added 25 cc. hydrochloric acid. Hydrogen sulphide was passed through these flasks from the Kipp generator for at least an hour. Precipitation seemed to be complete. The flasks were stoppered and allowed to stand over night.

The precipitates were filtered and washed with the washing solution, before described, until free from chloride. The test was made by boiling about 15 cc. of washings until hydrogen sulphide

and most of the alcohol was gone, diluting with water, and adding silver nitrate solution. About the usual amount of washing was required.

The precipitates were ignited directly to form germanium dioxide in the manner previously discussed. (See "Determination of Germanium", page 41, Final Method). To the residue in the crucible was added a few drops of sulphuric acid (1:1), then two-thirds of a crucible full of hydrochloric acid. The solution was evaporated to sulphur dioxide fumes. Hydrochloric acid was again added and evaporation was continued until sulphur dioxide fumes were driven off. The crucible was ignited, ammonium carbonate was added, and then ignition was continued, gently at first, finally for 10 min. at full heat of a Bunsen burner. This treatment was repeated to constant weight.

The residue in the distilling flask was transferred to an Erlenmeyer flask. A white crystalline solid was noted. It was probably lead chloride as it was completely soluble in hot water. The volume was made up to 200 cc., ammonium hydroxide being added to give a concentration of 1:3. Hydrogen sulphide was passed until the solution was saturated.

The black precipitate was filtered out. The yellow solution was acidified with sulphuric acid (1:1). One-sixth volume of sulphuric acid was added and the solution was saturated with hydrogen sulphide after being cooled to room temperature. The flask was stoppered and allowed to stand over night.

The precipitate was treated like those described above. The residue was labelled "Residue  $\text{NH}_4\text{HS}$  Extraction". The filtrate from this precipitate was saturated with hydrogen sulphide and allowed to stand several days. The precipitate was filtered and treated to form germanium dioxide. It was labelled "Residue from Filtrate".

Data:

No.	Distillate I		Percent Ge O <sub>2</sub>	Distillate II		Distillate III		Safety Flask		Residue NH <sub>4</sub> HS extraction		Residue from Filtrate	
	GaO <sub>2</sub> crude gms.	Residue evaporated with HCl and H <sub>2</sub> SO <sub>4</sub>		Evaporated with HCl and H <sub>2</sub> SO <sub>4</sub>		Evaporated HCl and H <sub>2</sub> SO <sub>4</sub>		Evaporated HCl and H <sub>2</sub> SO <sub>4</sub>		Weight Gr.	Spect- roscope test	Weight Gr.	Spect- roscope test
		Weight Gr.	Tests	Weight	Change Gr.	Tests Gate- house As	Weight	Change Gr.	Gate- house test				
1.	.0532	.0018	No Ge Zn Ba No As	.0009	+ .0001	.....	.0005	.0003	.....	.0015	+ .0001	.0019	Pb Zn Sn No Ge
2.	.0537	.0017	Zn No Ge No As	.0012	.0000	None	.0007	+ .0002	None	.0006	+ .0001	.0020	No Ge Zn Fe Pb Sn
3.	.0551	.0045	No Ge No As Na Zn Ge	.0014	.0000	None	.0005	+ .0003	None	.0006	+ .0001	.0586	No Ge Pb Na Sn
4.	.0514	.0043	N As Zn No As	With	Distillate I	.....	.0007	+ .0001	None	With Di- stillate I	.....	.1273	No Ge Pb
5.	.....	.....	Marsh test	With	Distillate I	.....	.0011	.....	None	With Di- stillate I	.....	.1397	No Ge Pb
6.	.0513	.0030	No As	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
7.	.0498	.0012	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
8.	.0531	.0045	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
9.	.0530	.0010	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
10.	(.0530)	.0017	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
11.	.0528	.0014	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

The residues after evaporation with hydrochloric and sulphuric acids were tested by means of the spectroscope. The remaining residue was tested by the Gatehouse test for arsenic.

In Nos. 4 and 5 the first and second distillates were caught in the same receiving flasks. To this was added the contents of the safety flask.

The corrections for solubility of germanium disulphide were made as usual on Nos. 1-5 but gave residues of the same weight as the ash of the filter papers.

Since no germanium was found in any of the second or third distillates or in the safety flasks, only the first distillation was made in Nos. 6-11.

In Nos. 1-8 the hydrogen sulphide generator worked intermittently and the results of the first precipitation were low. The corrections gave correspondingly high results but the necessary double precipitation may account for the slightly lower results.

In No. 10 volatilization occurred after the first ignition, due to a slight amount of carbon in the residue. The first residue showed a little dark color and should have been evaporated again with nitric acid. The figures in brackets were obtained from the first weighing and are probably nearer correct. That would make the result like Nos. 9 and 11.

**CONCLUSIONS.** The results show that germanium is completely distilled over by the one distillation with hydrochloric acid in a current of chlorine, after having been oxidized by passing chlorine through the potassium hydroxide solution. At the same time arsenic is completely retained.

Passing the distillate through a spiral condenser and then into water which is kept near the temperature where chlorine hydrate forms, retains the germanium chloride perfectly.

The germanium dioxide formed appears to contain some impurities. Whether or not this would be true with materials, which it is hoped may soon be obtained, is an open question. Much of the trouble appears to be due to impurities which have no necessary relationship to the method described.

Like silicon dioxide, germanium dioxide can be corrected for impurities by volatilization with a halogen acid.

## SUMMARY.

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Extraction of the "Germanium Concentrates" with water and ammonium sulphate solutions does not dissolve the germanium appreciably, thus indicating the probability that no free germanium dioxide is present but that the element exists as an insoluble compound with some of the accompanying elements. Its apparent insolubility suggests the value of further investigations.

The germanium was successfully extracted by dissolving in dilute sulphuric acid solution and was obtained as a pure compound by precipitating it from this solution with hydrogen sulphide, converting the sulphides to oxides with nitric acid, preparing potassium fluogermanate directly from these oxides by means of hydrofluoric acid and potassium fluoride, extracting the double fluoride with hot water, and twice recrystallizing. The separation was proven complete by a spectroscopic test and Marsh's test for arsenic; by evaporation with sulphuric acid thus converting to potassium sulphate and germanium dioxide, combined with the determination of water; and by the agreement between the determination of water and that of germanium.

Winkler's method of purification of germanium disulphide by fractional precipitation always gave an impure product containing zinc, arsenic, and usually cadmium. Germanium and arsenic are not separated by ignition even when an acid less volatile than the oxides of arsenic is used. The determination of germanium in the presence of arsenic by Winkler's method of fractional precipitation, which has been the method employed, appears, therefore, to be only an approximation made more accurate by the compensation of errors. The fact that ignition of pure germanic and arsenic oxides leaves much arsenic in the residue points to the formation of an arsenate of germanium.

Zinc and germanium are not separated by precipitating the latter with hydrogen sulphide from a solution made strongly acid (6 N) with sulphuric acid. The amount of zinc carried down is, apparently, too large to be accounted for by the phenomenon of adsorption and suggests as an explanation the formation of a thiogermanate, perhaps somewhat similar to argyrodite, and which probably is, at least, difficultly soluble in sulphuric and hydrochloric acids. Solu-

tion of the sulphides in ammonium sulphide effects a nearly quantitative separation of these metals, but the conditions for such separation need further investigation. Potassium and sodium sulphides do not give as good results.

Magnesia mixture precipitates from germanium solutions a white somewhat granular substance which contains magnesium and germanium, but no ammonium. It is nearly or quite insoluble in hot and cold water but easily soluble in dilute sulphuric acid. The formula was not determined but it appears to be a magnesium germanate.

Ammonium molybdate precipitates from dilute nitric acid solutions of germanium a yellow substance almost identical in appearance with ammonium arsenomolybdate. Its composition was not determined.

Zinc and sulphuric acid in the Marsh's test causes the evolution of germanium hydride as here no possibility of the formation of germanium chloride is present. The amount formed is, relatively, very small as most of the germanium, like tin, is precipitated in the generator. The element forms a brown film on the sides of the generator which is very characteristic. Germanium does not interfere with the test for arsenic, made by passing the gas from the Marsh's generator through silver nitrate solution. The arsenious sulphide obtained in the test contains no germanium.

Potassium fluogermanate, prepared as described, retains water even after drying several days at  $105^{\circ}\text{C}$ . This water is given off at a temperature of about  $500^{\circ}\text{C}$ ., causing decrepitation.

Potassium fluogermanate decomposes at about  $550^{\circ}\text{C}$ . in a current of dry air and at a little higher temperature when ignited in a closed crucible. It gives a sublimate which contains no potassium and which strongly attacks glass, thus indicating germanium tetrafluoride.

On evaporating potassium fluogermanate with dilute sulphuric acid no germanium tetrafluoride is volatilized. It would appear that the losses reported by Winkler were mechanical. Even the evaporation of 16 g. of the salt with dilute sulphuric acid gave no appreciable loss and afforded a direct method of decomposing the fluogermanate for the preparation of pure germanium dioxide. It also gives a direct method of determining germanium in the salt.

Methods are described for: the determination of water in potassium fluogermanate; the determination of germanium in potassium fluogermanate; the testing of the purity of this salt by evaporation

with sulphuric acid and weighing as potassium sulphate plus germanium dioxide; the determination of germanium in pure solutions; and the determination of germanium in the concentrates by distillation as germanium tetrachloride.

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